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# On the Activities of Coexisting Elements in Molten Iron. III The Activity of Mn in Molten Fe-Mn Alloy\*

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## Synopsis

By constructing the following electrode concentration cell and with a potentiometer, the authors measured the e.m.f. corresponding to the change in the Mn content in iron.



The temperature of the experiment was about  $1,590 \pm 5^\circ\text{C}$  and for the measurement of temperature, a Pt-Pt/Rh thermocouple was used. The theoretical relation between the e.m.f.,  $E(V)$  and the activity of Mn,  $a_{\text{Mn}}$  was as follows:

$$E = RT/nF \times \ln a_{\text{Mn}}^i / a_{\text{Mn}} - RT/nF \times \ln a_{\text{Mn}}^i / a'_{\text{Mn}} \quad (1)$$

where  $a_{\text{Mn}}^i$  = the activity of Mn ion in the molten slag

$a'_{\text{Mn}}$  = the activity of pure Mn

When pure Mn was selected so as to be in a standard state, the following equation was obtained from eq. (1):

$$E = -0.0002T/n \times \log a_{\text{Mn}} \quad (2)$$

$n$  was approximately determined as  $n=2$  by a calculation from the authors data. From eq. (2) the activities of Mn were determined all over the range. From the authors result, Fe-Mn binary solution was recognized to be an approximately ideal solution all over the range. Judging from consideration made from several points of view, Fe-Ni and Fe-Co binary solutions were also considered to follow the Raoult's law as in the case of Fe-Mn binary solution.

## I. Introduction

In order to know the behaviors of coexisting elements, such as C, Si, Mn, P, S, and O in molten iron, it is necessary to know the activity and activity coefficient of each element in molten iron. For example, in Fe-S binary system, the activity of S decreases as the concentration of S increases. However, C, Si and P are found in this system, the activity coefficient of S increases. In other words, these elements increase the fugacity of S, making it to be easily desulphurized. Expressing this relation quantitatively, it can be seen that in a pig iron whose composition is C = 3.75%, S = 0.15%, Si = 1.20% and Mn = 2.0%, the activity coefficient of S is about 5, showing it to be desulphurized about 5 times as easily as in the case of Fe-S or low carbon steel<sup>(1)</sup>. It is only in Fe-S system that such a quantitatively relation is known, and it will be an important step in steelmaking process if the activities or activity coefficients of elements other than S can be found. In practical iron and steel making, they show heterogeneous phase and that of multiple system,

\* The 65th report of the Research Institute of Mineral Dressing and Metallurgy.

(1) J. Chipman, Metal Progress, 61 (1952), 27.

but we can proceed to the study of the binary system and gradually to that of multiple system. With such an idea in mind, authors have already finished measurements of the activity of C and Si in Fe-C<sup>(2)</sup> and Fe-Si<sup>(3)</sup> system respectively. There are many studies made on the behaviors of Mn, chiefly from deoxidation equilibrium or from desulphurizing reaction, but no systematic measurements have ever been made on the behavior of Fe-Mn system as metallic solution. Making considerations on the basis of experimental results or thermodynamic data obtained hitherto, Fe-Mn system may be an ideal solution, on which authors made actual measurements over the whole range for further examination. Further, Mn, Ni, and Co are the elements similar to one another and Fe-Ni, and Fe-Co solutions may be regarded to have the same behaviors as Fe-Mn solution.

## II. Experimental procedure

The details of the experiment are omitted as they have been given in first report<sup>(2)</sup>. The following concentration cell was constructed for the present experiment.



That is to say, electrolytic Mn was used as the standard electrode, Fe-Mn alloys containing various kinds of Mn as other electrode and slag containing MnO as intermediate electrolyte. The crucible consists of MgO crucible whose shape is shown in Fig. 1. This crucible was made in our laboratory as follows: Commercial magnesia was heated in a graphite crucible at about 1,500°C for about 60 minutes and crushing it in 60 mesh, it was solidified in a graphite crucible in the form desired as shown in Fig. 1. In doing this, it is necessary to add some water. Then it was further heated together with a graphite crucible in a high frequency induction furnace up to 1,800°-1,900°C. Care should be taken not to heat it intensely from the beginning, but to heat it slowly. The intense heating at the initial stage will cause cracks. The crucible thus made must be kept in a desiccater. In making measurement, the MgO crucible should be put again in the graphite crucible and heated slowly to the temperature above required. Then a Fe-Mn alloy containing X quantity of Mn is put in the side of A and the electrolytic Mn in the side of B. After A and B are melted, a slag containing MnO which has been adjusted previously is added through a 10 mm quartz tube to make it an intermediate electrolyte in the part of C. The synthetic slag is obtained by melting highly pure MnO, SiO<sub>2</sub> and CaO in a MgO or Al<sub>2</sub>O<sub>3</sub> crucible, and the slag after cooling shows black-brown colour. On reaching

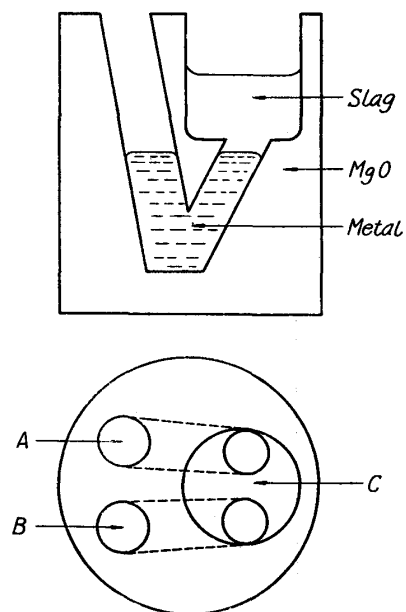


Fig. 1. The cell design.

(2) K. Sanbongi, M. Ohtani, Sci. Rep. RITU, A5 (1953), 263.

(3) K. Sanbongi, M. Ohtani, ibid., A5 (1953), 350.

the temperature required, the W wire is put into both A and B sides and the e.m.f. between them is measured with a potentiometer. While doing this, the W wire can be prevented from melting if it can be kept at about the same temperature as the molten iron at the point it is inserted and if the time for measurement is shortened. After finishing measurements, if the crucible is found undamaged, another measurement can be made by adding Mn or Fe to the side of A. Knowing the fact that the diffusion velocity of Mn in molten iron is slow, authors made measurements after a sufficient lapse of time after the addition of Mn. After making measurement, specimens required for analysis were sucked up with a syringe with quartz capillary. Pure iron used is composed of C=0.03%, S=0.013%, P=0.004%

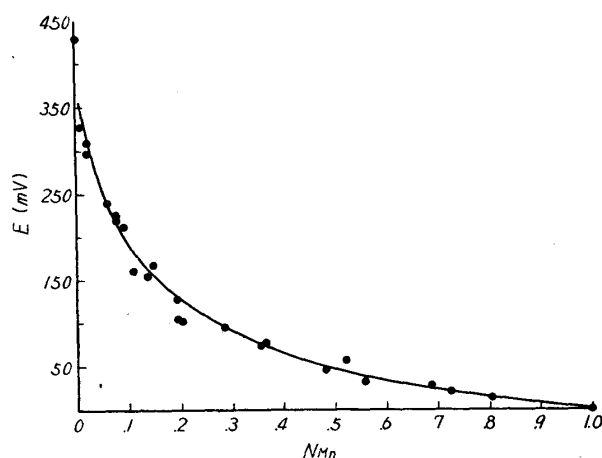


Fig. 2. Relation between e.m.f. and mole fraction of Mn.

and the result of analysis of electrolytic Mn is 99.9%. Analysis of Mn was carried out chiefly by means of bismuthate method and the spectrophotometer was also used in the analysis.

### III. Experimental results

The results of the experiment are summarized in Table 1. Fig. 2 shows the relation between the e.m.f. (mv) and mole fraction of Mn,  $N_{Mn}$ . The following equation holds between

Table 1. Experimental data.

No.	Mn (%)	$N_{Mn}$	e.m.f. (v)	$a_{Mn}$	Note
3	0.77	0.0078	0.2950	0.027	SiO <sub>2</sub> 54% MnO 8.4% CaO 29.0% MgO 8.4%
4	8.95	0.091	0.2123	0.074	
5	19.18	0.194	0.1020	0.285	
7	pure		0	1	
8	1.15	0.012	0.310	0.022	SiO <sub>2</sub> 50% CaO 30% MnO 10% MgO 10%
10	27.70	0.280	0.0933	0.330	
11	13.36	0.134	0.1550	0.148	
12	19.35	0.196	0.1250	0.215	
13	47.42	0.480	0.0408	0.605	
14	54.31	0.550	0.0327	0.669	
15	79.47	0.80	0.0150	0.832	
18	1.20	0.013	0.3307	0.017	
20	7.76	0.079	0.2202	0.067	
21	10.37	0.104	0.1597	0.140	
25	67.53	0.680	0.0305	0.660	
28	4.68	0.048	0.2420	0.051	
29	6.93	0.070	0.1825	0.106	
30	0.38	0.004	0.4350	0.006	
31	14.42	0.146	0.1664	0.129	
33	19.51	0.198	0.1019	0.286	
35	52.18	0.524	0.0648	0.452	
37	36.45	0.368	0.0836	0.358	
38	35.11	0.355	0.0711	0.418	
39	71.40	0.717	0.0232	0.752	

the e.m.f.,  $E$  and the activity of Mn,  $a_{\text{Mn}}$ :

$$\begin{aligned} E &= RT/nF \times \ln a_{\text{Mn}}^i/a_{\text{Mn}} - RT/nF \times \ln a_{\text{Mn}}^i/a'_{\text{Mn}} \\ &= RT/nF \times \ln a'_{\text{Mn}}/a_{\text{Mn}} \end{aligned} \quad (3.1)$$

where

$a_{\text{Mn}}$  = the activity of Mn in Fe-Mn binary system

$a'_{\text{Mn}}$  = the activity of pure Mn

$a_{\text{Mn}}^i$  = the activity of Mn ion in molten slag

When pure Mn is selected as in the standard state,  $a'_{\text{Mn}} = 1$ , and consequently, eq. (3.2) may be deduced from eq. (3.1) as follows:

$$E = -RT/nF \times \ln a_{\text{Mn}} \doteq -0.0002T/n \times \log a_{\text{Mn}} \quad (3.2)$$

In this formula,  $n$  is determined in the same manner as in the previous report<sup>(3)</sup> and  $N_{\text{Mn}} = a_{\text{Mn}}$  holds where the concentration of Mn is low and from the results of the experiments,

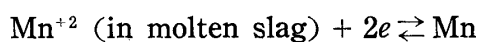
$$E_1 = -RT/nF \times \ln N_1 \quad (3.3)$$

$$E_2 = -RT/nF \times \ln N_2 \quad (3.4)$$

(3.3)-(3.4)

$$\begin{aligned} E_1 - E_2 &= -RT/nF \times \ln N_1/N_2 \\ &\doteq -0.0002T/n \times \log N_1/N_2 \end{aligned} \quad (3.5)$$

Substituting  $N_1 = 0.039$ ,  $E_1 = 0.4350$ ,  $N_2 = 0.013$ ,  $E_2 = 0.3307$  and  $T = 1,873^\circ\text{K}$  in eq. (3.5),  $n$  is found to be  $n = 1.9$  approximately  $n = 2$ . Consequently, the cell reaction in the present experiment may be regarded to be as follows:



By substituting  $n = 2$  thus obtained and values of  $T$  and  $E$  in eq. (3.2),  $a_{\text{Mn}}$ , corresponding to  $N_{\text{Mn}}$ , can be obtained. Fig. 3 shows such relationships.

## VI. Consideration

### 1. Behavior of Mn in Fe-Mn binary solution

It has been said for a long time that Mn in molten iron is an ideal solution<sup>(4)</sup> and recently Chipman<sup>(5)</sup> tried to find changes in free energy produced when various elements melt into Fe and said that Fe-Mn binary solution might be regarded as an ideal solution by giving eq. (4.1) in the case of Mn,

$$\begin{aligned} \text{Mn}(l) &= \text{Mn} \quad \Delta F^\circ = -9.11T \\ r_{1,873^\circ\text{K}}^\circ &= 1 \end{aligned} \quad (4.1)$$

In this equation,  $r^\circ$  is the activity coefficient of Mn at infinite dilution,

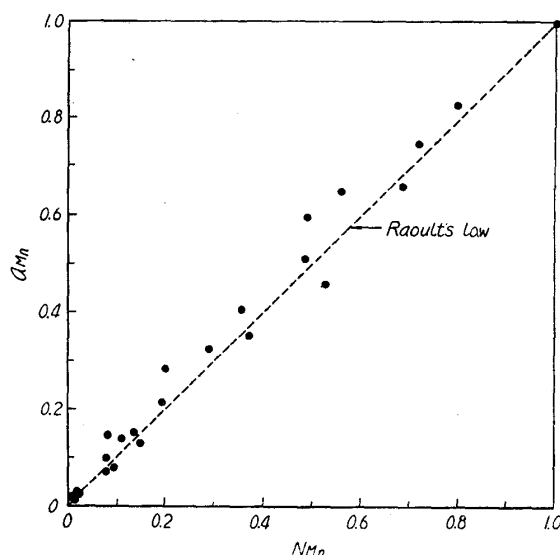


Fig. 3. Relation between activity of Mn,  $a_{\text{Mn}}$  and mole fraction of Mn,  $N_{\text{Mn}}$ .

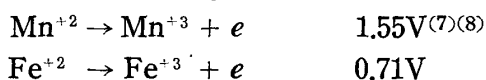
(4) F. Körber, W. Oelsen, Mitt Kais. Wil. Inst. Eisenforschung. 14 (1932), 181.

(5) J. Chipman, Basic Open Hearth Steelmaking. 1951. (A.I.M.E.) 638.

i.e. indicates the inclination of the curve of the solution made in accordance with Henry's law. When it is equal to 1, it follows Raoult's law, being the ideal solution. Kitchener<sup>(6)</sup> says from the view of atomic structure that Fe-Mn solutions may show slight non-ideality. As shown in Fig. 3, each point lies near to the straight line predicted by Raoult's law, but within the margin of experimental error they are in agreement with Raoult's law. That is, Fe-Mn solution is considered to form an ideal solution approximately.

## 2. Mn ions in molten slag

It has been stated that molten slag containing MnO dissociate into ions and that Mn ion is bivalent. Although there is no experimental fact to ascertain whether the existence of ions with different values such as  $\text{Mn}^{+3}$  should be recognized or not, or whether the reaction  $\text{Mn}^{+2} \rightleftharpoons \text{Mn}^{+3}$  should take place in the solution at high temperature or not, an investigation into the standard electrode potential in the aqueous solution shows the following values;



This shows that the coexistence of  $\text{Mn}^{+2}$  and  $\text{Mn}^{+3}$  is less probable than that of  $\text{Fe}^{+2}$  and  $\text{Fe}^{+3}$ . That  $\text{Fe}^{+2}$  and  $\text{Fe}^{+3}$  coexist when iron oxide is treated at high temperature is a fact that has already been recognized.<sup>(9)(10)</sup> Authors obtained the result that  $n$  was equal to 2 in molten slag but it is rash to extend the results

obtained the experiments with aqueous solution to those obtained at high temperature. Considering, however, these results in comparison with those obtained at high temperature, this relation may be regarded to hold qualitatively. That is to say, it is less probable that  $\text{Mn}^{+2}$  and  $\text{Mn}^{+3}$  coexist in molten slag.  $\text{Mn}^{+2}$  is considered to exist as such. Bockris and others<sup>(8)</sup> who measured electro-conductivity expressed the same opinion as authors.

## 3. Behaviors of Fe-Co and Fe-Ni binary solutions

Mn, Co, and Ni are the elements similar to iron and their binary diagrams are also similar to one another as shown in Fig. 4. Co, Ni and Mn

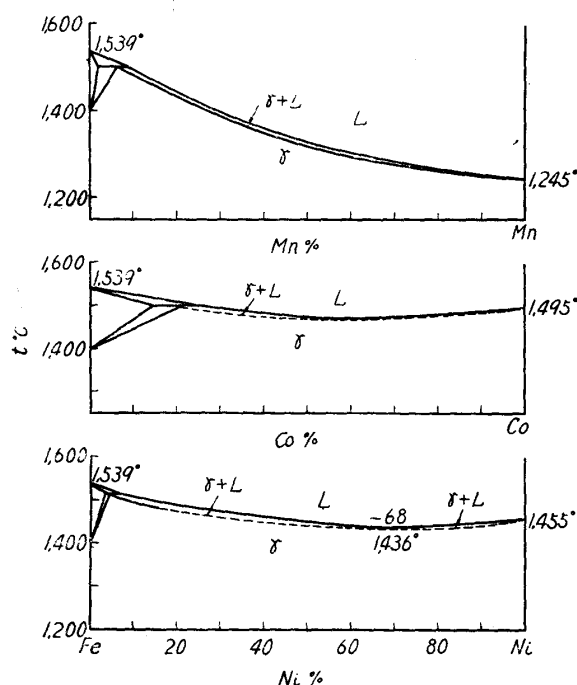


Fig. 4. Phase diagram, Fe-Mn, Fe-Co, Fe-Ni (upperside)

- (6) J. A. Kitchener, *Iron and Steel*, 27 (1954), 473.
- (7) W.H. Latimer, *Oxidation States of the Elements and Their Potentials in Aqueous Solutions*, (1938)
- (8) J. O'M. Bockris, J. A. Kitchener, A. E. Davies, *Trans. Faraday. Soc.*, 48 (1952), 546.
- (9) F. D. Richardson, *Discussions of Faraday Soc.* 4 (1948), 244.
- (10) J. Chipman, H. Larson, *Am. Inst. Min. Met. Engrs.*, (1952), 1089.

give a complete series of substitutional solid solutions with  $\gamma$ -Fe. The degree of similarity of these metals to Fe can also be observed by the metallic radii as shown in Table 2.

Table 2. Several properties of metals.

Element	Cr	Mn	Fe	Co	Ni
Atomic number	24	25	26	27	28
Atomic weight	52.01	54.93	55.84	58.94	58.69
Atomic radius (Å. C. N=12) <sup>(11)</sup>	1.357 1.267	1.306 1.261	1.260	1.252	1.244

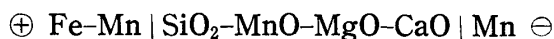
Jander and Krieger<sup>(12)</sup>, Jander and Senf<sup>(13)</sup> described that molten Fe-Ni and Fe-Co system form the ideal solution over the whole range and Oriani<sup>(14)</sup> reported the same result on solid Fe-Ni system. According to Kubaschewski and Goldbeck<sup>(15)</sup>, Ni in Fe tends to show almost an ideal behavior. The following free energies were given recently by Chipman<sup>(5)</sup>;

$$\begin{array}{lll}
 \Delta F^\circ & & T_{1,873^\circ\text{K}} \\
 \text{Ni (l)} = \underline{\text{Ni}} & -9.21T & 1 \\
 \text{Co (l)} = \underline{\text{Co}} & -9.26T & 1
 \end{array}$$

These relations are similar conclusions as in the case of Mn. At the present time direct evidence about these solutions is lacking but taking these considerations into account, it seems very likely that Fe-Co and Fe-Ni solutions will be ideal, i.e., follow Raoult's law closely.

## V. Conclusion

1. By constructing an electrode concentration cell given below, authors measured the e.m.f. over the whole range of Fe-Mn system and obtained the result that Fe-Mn system approximately follows Raoult's law.



The measurements were carried out at temperatures in the neighborhood of  $1,590 \pm 5^\circ\text{C}$ .

2. In the range of composition studied, Mn ions in the molten slag containing MnO are considered to be  $\text{Mn}^{+2}$ , on which some considerations have been given.

3. It is considered that Fe-Co and Fe-Ni systems follow Raoult's law over the whole range.

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(11) L. Pauling, J. Am. Chem. Soc., **69** (1947), 542.

(12) W. Jander, A. Krieger, Z. anorg. allg. Chemie, **232** (1937), 39.

(13) W. Jander, H. Senf, *ibid.*, **216** (1933), 316.

(14) R. A. Oriani, Acta Meta., **1** (1953), 448.

(15) O. Kubaschewski, O. Goldbeck, Trans. Faraday Soc., **45** (1949), 948.